



Forms and exchangeability of inorganic phosphate in composted solid organic wastes

E. Frossard^{1,*}, P. Skrabal², S. Sinaj¹, F. Bangerter² & O. Traore¹

¹Group of Plant Nutrition, Institute of Plant Sciences, Swiss Federal Institute of Technology (ETH), Research Station Eschikon, Postfach 185 CH-8315 Eschikon-Lindau, Switzerland; ²Institute of Polymers and Laboratory of Technical Chemistry, Department of Chemistry, ETH, CH-8092 Zurich, Switzerland (*Corresponding author; e-mail: emmanuel.frossard@ipw.agrl.ethz.ch)

Received 11 May 2000; accepted in revised form 4 December 2000

Key words: calcium phosphates; compost, isotopic exchange, MAS ³¹P NMR, phosphorus, sequential extraction

Abstract

Switzerland yearly produces more than 260,000 Mg of compost, two thirds of which is recycled in agriculture and horticulture. This research was undertaken to examine the forms and availability of inorganic P (Pi) in Swiss composts made from solid kitchen and garden wastes using the isotopic exchange kinetic technique, a sequential Pi extraction and magic angle spinning (MAS) solid-state ³¹P nuclear magnetic resonance (NMR) spectroscopy. The different approaches described in this paper demonstrate the presence of a complex mixture of Pi species in the studied composts. Isotopic exchange experiments and sequential extraction showed that these composts contained relatively large concentrations of rapidly available Pi. Significant correlations were observed between the concentration of water-soluble Pi (Cp), and the total N, C and P content of composts suggesting that organic substances partly controlled the amount of rapidly available Pi. Significant correlations were observed in alkaline composts between the amount of Pi which can not be exchanged within 3 months and the total P and Ca content. In alkaline composts solid-state MAS ³¹P NMR results suggested the presence of a range of slightly soluble and poorly crystallized Ca-P compounds such as apatites or octacalcium phosphates and of organic P compounds. The slowly or non-exchangeable Pi present in these composts could therefore be bound to Ca in the form of apatites or octacalcium phosphates.

Introduction

Switzerland yearly produces more than 260,000 Mg compost (Candinas et al., 1999) from solid organic wastes, such as kitchen and garden wastes, which are separated at the household or industry level from other wastes and are collected by compost producers. About two thirds of the compost are then recycled in agriculture and horticulture (Candinas et al., 1999). The understanding of compost properties is important to optimize its recycling. Intensive research has been conducted on the forms of organic matter in composts and its mineralisation once added to the soil (Sikora and Yakovchenko, 1996; Gigliotti et al., 1999) and on the release of N or metals from composts to agricultural crops (Warman et al., 1995; Hadas et al., 1996;

Wen et al., 1999). Less information exists on the form of phosphorus (P) in composts and on its availability to plants (Preston et al., 1986; Wen et al., 1997; Kuo et al., 1999).

To date the research on P in composts has focussed on studying P extractability using a range of chemical extractants to estimate P forms and availability to plants and on assessing P uptake by plants from various soil/compost mixtures. The amount of P which can be extracted from composts varies from 3% of total P when water is used, up to 98% when strong acids such as citric acid or HCl are used (Pommel, 1982; Kuhn et al., 1996). Kuo et al. (1999) and Traore et al. (1999) recently used sequential extractions for characterizing P forms in different compost types. These investigations suggest the presence of relatively insol-

uble calcium phosphates in alkaline composts (Preston et al., 1986; Traore et al., 1999). In neutral or acidic fishwaste composts Fe and Al species could also control the inorganic P concentration in solution (Kuo et al., 1999). A single study of P forms with ^{31}P NMR spectroscopy showed the presence of orthophosphate, calcium phosphate and organic phosphate in composts prepared from peat and wastes of the fish and crab processing industry (Preston et al., 1986). Use of isotopic exchange kinetics suggests that compost inorganic P (Pi) is composed of a continuum of Pi species, some of them are very rapidly exchangeable with Pi in the solution, while a majority of them are slowly or not at all exchangeable with Pi in the solution (Traore et al., 1999). The amount of P taken up by a plant from a soil/compost mixture has been shown to vary from 10 to 264% of the amount of P taken up from a water-soluble mineral fertilizer at comparable P application rates (Pommel, 1982; Sikora et al., 1982; Bezzola et al., 1994). This large variability is partly related to the differences in compost properties but also to the various methodologies and systems (plant species, soil types) used in these studies. This paper examines the forms and availability of inorganic P in Swiss composts from solid organic wastes while the fate of compost-P in soil/plant systems is studied in the following paper (Sinaj et al., 2001). In the present work, the forms and availability of Pi from a collection of composts are studied (i) by assessing the exchangeability of inorganic P using the isotopic exchange kinetic technique as proposed by Traore et al. (1999), (ii) by correlation analysis between selected chemical characteristics of the composts and the amount of P exchangeable after various times, (iii) by sequentially extracting Pi forms and (iv) by using MAS solid-state ^{31}P NMR spectroscopy to characterize P species in unextracted compost samples, and after various steps of the sequential extraction.

Material and methods

Composts

Sixteen composts were collected. The origin of each compost, the composted materials, and the composting processes are summarized in Table 1. Samples were taken from at least five points along each compost row just after it was turned, and from at least five points at 50 cm depth in each pile. The samples were then homogenized, dried at 20 °C and sieved at 2 mm.

Analysis

Total nitrogen and carbon were analyzed with a Carlo Erba C/N analyzer. The total Ca, Mg, Fe and Al were extracted from ash with hot concentrated (11.3 M) HCl after sample ignition at 600 °C during 6 hours, and measured by Inductively Coupled Plasma-Atomic Emission Spectroscopy. The total P content of composts was measured after digestion in hot concentrated (11.6 M) HClO_4 . The organic P content was determined according to Saunders & Williams (1955) and the inorganic P was calculated as the difference between total P and organic P. These data and the pH of the composts are given in the Table 2.

The sequential Pi extraction of Traore et al. (1999) was carried out with composts 1, 2, 8 and 14 at a compost/solution ratio of 1:200 (g:ml). Samples were first extracted with distilled water, followed by NaHCO_3 (0.5 M at pH 8.5), by NaOH (0.1 M) and finally by HCl (1 M). Each extraction was carried out during 16 h. After each extraction the supernatant liquid was separated from the solid by centrifugation and filtration through a 0.2 μm membrane and its inorganic P concentration determined using a colorimetric method (John, 1970). According to Frossard et al. (1996), water and NaHCO_3 extractable Pi is rapidly plant available, NaOH extractable Pi is bound to Fe or Al oxides or to organic substances and HCl extractable Pi is associated with calcium in the form of slightly soluble compounds such as apatites or octacalcium phosphate. The amount of residual Pi was calculated as the difference between total Pi and the amount of Pi extracted with water, NaHCO_3 , NaOH and HCl.

Isotopic exchange kinetics

The theory underlying the use of this method has been described before (Fardeau, 1996). When $^{33}\text{PO}_4^{3-}$ is added carrier-free to a compost-solution system at a steady-state the radioactivity in solution decreases with time t (in minutes) according to Equation (1) (Traore et al., 1999),

$$\frac{r(t)}{R_0} = \frac{[r_{1\text{min}}]}{R_0} \times t^{-n}, \quad (1)$$

where R is the total introduced radioactivity (MBq); $r_{1\text{min}}$ and $r(t)$ are the radioactivity (MBq) remaining in the solution after 1 and t minutes, respectively; and n describes the rate of disappearance of the tracer from the solution after 1 min.

The quantity $E(t)$ (g P kg^{-1} dry matter compost) of isotopically exchangeable phosphate at a time t can

Table 1. Origin, substrates, and composting processes used in the fabrication of the studied composts

| Compost | Origin | Substrate | Process | Duration |
|---------|------------|---|---|------------|
| 1 | Eglisau | Solid urban organic wastes | Composted in pile, turned over each 2nd week | 6 weeks |
| 2 | Zurich | Solid urban organic wastes | Semi-anaerobic digestion for 2 weeks and aerobic for 6 weeks, stabilization with lime | 8 weeks |
| 3 | Zurich | Solid urban organic wastes | Semi-anaerobic digestion for 2 weeks and aerobic for 4 weeks, stabilization with lime | 6 weeks |
| 4 | Fehraltorf | Solid urban organic and woody wastes | Composted in row, turned over once a week | 10 weeks |
| 5 | Fehraltorf | Solid urban organic and woody wastes | Composted in row, turned over once a week | 9 weeks |
| 6 | Fehraltorf | Garden and woody wastes, farmyard manure | Composted in pile, low pressure forced aeration | 18 days |
| 7 | Fehraltorf | Solid urban organic wastes | Composted in row, turned over once a week | 14 weeks |
| 8 | Fehraltorf | Solid urban organic and woody wastes, farmyard manure | Composted in row, turned over every 2nd day | 6 months |
| 9 | Fehraltorf | Solid urban organic and woody wastes | Composted in row, turned over once a week | 9 weeks |
| 10 | Fehraltorf | Solid urban organic and woody wastes | Composted in row, turned over once a week | 10 weeks |
| 11 | Fehraltorf | Solid urban organic and woody wastes, farmyard manure | Composted in row, turned over once a week | 14 weeks |
| 12 | Fehraltorf | Woody wastes | Composted in row, turned over once a week | 18 weeks |
| 13 | Fehraltorf | Solid urban organic wastes | Composted in row, turned over once a week | 4 weeks |
| 14 | Leibstadt | Solid urban organic wastes, coco nut fibers | Composted in pile (semi-anaerobic) | 7 months |
| 15 | Leibstadt | Solid urban organic wastes, and rice straw | Composted in pile (semi-anaerobic) | 6.5 months |
| 16 | Leibstadt | Solid urban organic and woody wastes | Composted in pile (semi-anaerobic) | 2 years |

Table 2. pH, total C, N, Ca, Fe, Al, Mg, P and total inorganic P concentrations (g kg^{-1} DM) in the studied composts

| Compost | pH | C | N | Ca | Fe | Al | Mg | Total P | Inorganic P |
|---------|-----|-------|------|-------|------|------|------|---------|-------------|
| 1 | 8.8 | 232.4 | 16.6 | 42.9 | 10.7 | 11.6 | 6.3 | 3.24 | 2.75 |
| 2 | 8.6 | 189.6 | 13.1 | 183.9 | 4.1 | 3.9 | 6.4 | 3.40 | 2.99 |
| 3 | 8.0 | 265.0 | 13.8 | 107.0 | 6.5 | 5.9 | 8.2 | 3.44 | 2.70 |
| 4 | 8.4 | 173.7 | 12.3 | 38.1 | 12.7 | 11.9 | 8.5 | 2.96 | 1.91 |
| 5 | 7.7 | 185.9 | 9.7 | 44.7 | 15.5 | 13.7 | 8.7 | 3.43 | 1.97 |
| 6 | 8.2 | 305.6 | 14.7 | 34.6 | 8.9 | 8.9 | 5.5 | 3.94 | 2.15 |
| 7 | 8.2 | 216.2 | 13.1 | 42.6 | 12.0 | 11.8 | 9.4 | 2.25 | 2.14 |
| 8 | 8.8 | 162.3 | 13.8 | 44.5 | 14.8 | 13.8 | 10.3 | 3.75 | 2.52 |
| 9 | 7.7 | 214.1 | 11.0 | 39.3 | 13.6 | 11.7 | 8.7 | 2.53 | 1.53 |
| 10 | 8.4 | 175.9 | 12.2 | 38.9 | 11.5 | 12.0 | 7.7 | 3.08 | 2.05 |
| 11 | 8.4 | 172.5 | 13.0 | 44.0 | 15.3 | 12.8 | 10.0 | 3.44 | 2.26 |
| 12 | 7.6 | 157.1 | 8.2 | 42.5 | 16.4 | 13.8 | 12.3 | 2.61 | 1.53 |
| 13 | 6.3 | 301.6 | 26.4 | 44.2 | 6.3 | 5.9 | 7.2 | 7.19 | 5.08 |
| 14 | 8.0 | 169.3 | 8.3 | 115.0 | 15.1 | 8.5 | 6.8 | 4.78 | 3.71 |
| 15 | 8.2 | 188.8 | 11.6 | 70.2 | 11.2 | 9.9 | 5.0 | 3.04 | 2.06 |
| 16 | 7.4 | 87.8 | 6.6 | 19.5 | 9.8 | 8.9 | 3.3 | 2.09 | 1.59 |

be calculated by Equation (2), assuming that $^{31}\text{PO}_4^{3-}$ and $^{33}\text{PO}_4^{3-}$ ions have the same fate in the studied system.

$$E(t) = 100 \times C_p \times \frac{[R_0]}{r(t)} \times t^n \quad (2)$$

In (2) C_p is the concentration of water-soluble phosphate (g P l^{-1}). The factor of 100 arises from the compost/solution ratio of 1 g dry matter of compost in 100 ml of water so that $100 \times C_p$ is equivalent to the water-soluble phosphate content of the compost expressed in g P kg^{-1} . Isotopically exchangeable phosphate was divided into three pools as described by Traore et al. (1999): the pool of free phosphate that was approximated by the quantity $E_{1\text{min}}$ of phosphate isotopically exchangeable within 1 min, the pool of phosphate exchangeable between 1 min and 3 months $E_{1\text{min}-3\text{mo}}$ and the pool of phosphate that is not isotopically exchangeable within 3 months $E_{>3\text{mo}}$. The amount of P present in the pool $E_{1\text{min}-3\text{mo}}$ was calculated as the difference between $E_{3\text{mo}}$ and $E_{1\text{min}}$, which themselves were calculated with Equation (2). The amount of phosphate that can not be isotopically exchanged within 3 months $E_{>3\text{mo}}$ was calculated as the difference between the total inorganic P and the amount of P exchangeable within 3 months.

Compost/water suspensions with a compost/solution ratio of 1:99 (g:ml) were first shaken during 17 h. At $t = 0$ minute, 1 ml of solution containing 0.1 MBq carrier free $^{33}\text{PO}_4^{3-}$ diluted in water was introduced into the suspension, which was then stirred. Samples were taken from the suspension after 1, 10, 40 and 100 min, filtered through a $0.2 \mu\text{m}$ membrane and the radioactivity $r(t)$ remaining in the solution was analyzed by scintillation counting. The parameter n was deduced from linear regression analysis of $\log(r(t)/R_0)$ as a function of $\log(t)$. At the end of the experiment, the suspension was filtered through a $0.025 \mu\text{m}$ membrane and the Pi concentration in the solution (C_p) was measured by a colorimetric method (John, 1970).

Solid-state MAS ^{31}P NMR spectroscopy

All spectra were obtained on a Bruker AMX 400 WB spectrometer (9.395 T, 161.98 MHz for ^{31}P). Samples were spun in zirconium rotors (7 Mm OD) at the Magic Angle (54.74°) with 6, 7 or 8 kHz, respectively. Unless stated otherwise, compost samples were submitted to two types of pulse sequences: a single pulse sequence (SP, $3.5 \mu\text{s}$ pulse length, i.e. ca. 60° pulse angle) and a relaxation delay of 20 s for ^{31}P nuclei,

and a cross-polarization sequence (CP, contact time of 2 ms) with a relaxation delay of 3 s for ^1H nuclei. In both cases high-power proton decoupling was applied during the acquisition time. The single pulse sequence enabled to observe all types of ^{31}P nuclei present in the samples, while the CP sequence was used to selectively observe the ^{31}P nuclei located in close vicinity (within a few angstroms) of ^1H nuclei. Chemical shifts (δ in ppm) were measured relative to external $\text{NH}_4\text{H}_2\text{PO}_4$ which itself is observed 0.72 ppm downfield from external 85% aqueous H_3PO_4 . The given chemical shifts refer to H_3PO_4 at 0 ppm. Peaks were further characterized by their width at half-height ($\Delta\nu_{1/2}$ in Hz) and, for obtaining a very approximate measure of the P content (neglecting the various, possibly different relaxation times and/or the cross-polarization rates), by the signal/noise ratio (S/N) which was calculated from the usual equation (3).

$$S/N = 2.5 \times \text{peak height} / \text{maximum noise width} \quad (3)$$

Finely ground, air-dried samples of the composts 1, 2, 8 and 14 were analyzed in addition to the solid residues obtained after the first 3 steps (H_2O , NaHCO_3 and NaOH) of the sequential extraction of composts 1 and 2. For chemical shift comparisons also the solid-state ^{31}P NMR spectra of eight reference substances were measured: $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ (Fluka AG, 92% purity), $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ (Merck AG, quality extrapure), deoxyribonucleic acid from herring sperm (DNA, Sigma), myo-inositol hexaphosphate (I6P, Sigma, 90% purity), an hydroxyapatite from the Swiss canton of Uri (OHA), two fluoroapatites (FA1 and FA2) from the Swiss canton of Tessin, and a fluoroapatite (FA3) from a Florida phosphate rock (US National Institute of Standards and Technology).

Statistical analysis

Correlation analysis between chemical characteristics of the composts (Table 2) and the parameters obtained from the isotopic exchange experiments was done in the general linear regression model (SYSTAT 6.0, 1996). Average coefficients of variation (CV) of 5, 14, and 18% were obtained for $r_{1\text{min}}/R_0$, C_p and n , respectively. Average CV of 9, 13, 15, 6, and 22% were obtained for total P, inorganic P, $E_{1\text{min}}$, $E_{1\text{min}-3\text{mo}}$ and $E_{>3\text{mo}}$, respectively. The statistical significance indicated a 0.05 probability level.

Results and discussion

Total P and Inorganic P

Total P varied between 2.09 and 7.19 g kg⁻¹ dry matter (DM) with a mean value of 3.45 (Table 2). Inorganic P ranged between 54.6 and 95.1% of the total P with a mean value of 70.6%. These results are in agreement with those reported in literature for fresh and air-dried composts (Preston et al., 1986; Kuhn et al., 1996; Kuo et al., 1999; Traore et al., 1999) and confirm that the larger part of the P content in composts is present in inorganic forms. However as air-drying of plant litter or organic matter-rich soils induces the release of orthophosphate to the solution due to organic and microbial P mineralisation (Grierson et al., 1998), air-drying might have resulted in a slight overestimation of mineral P forms in composts.

Pi exchangeability

The proportion of radioactivity remaining in solution after 1 min of isotopic exchange (r_{1min}/R_0) ranged between 0.8 and 1.0. The rate of radioactivity decrease from the solution after the 1st minute of exchange (n) was between 0.02 and 0.06, except 0.10 and 0.17 for composts 16 and 14, respectively (Table 3). The mean concentration of Pi in solution (Cp) reached 3.05 mg P l⁻¹ representing in average 8.8% of the total P. The proportion of Pi isotopically exchangeable within 1 min, E_{1min} , varied between 2.5 and 16.4% of total P. The proportion of Pi isotopically exchangeable between 1 min and 3 months, $E_{1min-3mo}$, varied between 3.1 and 17.1% of total P. Finally the proportion of Pi which could not be isotopically exchanged within 3 months, $E_{>3mo}$, varied between 40.9 and 77.3% of compost total P.

These results show that in comparison to soils, composts contain a relatively large fraction of Pi ions that are instantaneously available to plants. However, the largest fraction of Pi species is trapped in physico-chemical environments which strongly hinder their exchangeability with solution-Pi.

Relation between Pi exchangeability and some chemical properties of composts

The parameters r_{1min}/R_0 and n showed too little variation in this group of composts to be studied by correlation analysis. There is a positive correlation between the concentration of Pi in the solution (Cp) and the total N content (Figure 1). Linear correlations,

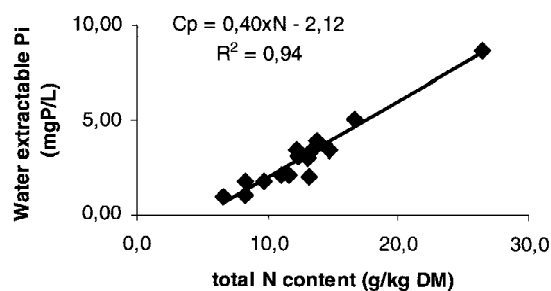


Figure 1. Relation between the concentration of water-extractable inorganic P (Cp) in composts and their total N content.

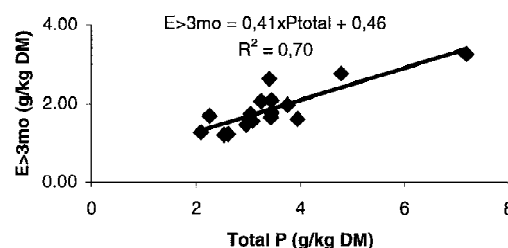


Figure 2. Relation between the total P content (total P) and the calculated amount of Pi which can not be isotopically exchanged within 3 months ($E_{>3mo}$) in the studied composts.

although with much lower coefficients, were also observed between Cp and total C ($r^2=0.48$) and between Cp and total P ($r^2=0.47$). Similar correlations were obtained between the total contents of C, N and P and E_{1min} since the ratio r_{1min}/R_0 varied between 0.8 and 1.0. These results suggest that the amount of organic matter in the composts controls the concentration of Pi in the solution. This could be due to (i) the composition of the organic wastes themselves since these are the original sources of N and P of the composts (while some of the C was added in composts 2 and 3 as lime during composting), (ii) to the inhibitory effect of organic substances on the precipitation of Pi in insoluble forms such as apatite or octacalcium P (Inskeep and Silvertooth, 1988), and/or (iii) to mineralisation of organic and microbial P caused by air-drying the composts before analysis (Grierson et al., 1998). The observed correlation between total N and Cp is strong enough to use the total N for this type of composts as a predictor for the amount of rapidly plant-available Pi.

The quantity of P, which could not be exchanged within 3 months $E_{>3mo}$, is positively correlated to total P (Figure 2) and total Ca (Figure 3). The outlier which is encircled in Figure 3, is the only compost exhibiting a pH lower than 7. A weak positive correlation was also observed between $E_{>3mo}$ and total N ($r^2=0.40$), while a weak negative relation was observed between

Table 3. Fraction of radioactive P remaining in the solution after 1 min of isotopic exchange (r_{1min}/R_0), factor describing the disappearance of radioactive P from the solution after 1 min of isotopic exchange (n), concentration of Pi in the solution (Cp, mg l⁻¹), quantity of P (g kg⁻¹ DM) isotopically exchangeable within 1 min (E_{1min}), exchangeable between 1 min and 3 months ($E_{1min-3mo}$), not exchanged within 3 months ($E_{>3mo}$) in the studied composts

| Compost | r_{1min}/R_0 | n | Cp | E_{1min} | $E_{1min-3mo}$ | $E_{>3mo}$ |
|---------|----------------|------|------|------------|----------------|------------|
| 1 | 0.96 | 0.02 | 5.05 | 0.53 | 0.16 | 2.06 |
| 2 | 0.97 | 0.05 | 1.99 | 0.21 | 0.16 | 2.63 |
| 3 | 1.00 | 0.04 | 3.92 | 0.39 | 0.22 | 2.09 |
| 4 | 0.98 | 0.03 | 3.03 | 0.31 | 0.14 | 1.46 |
| 5 | 0.95 | 0.05 | 1.73 | 0.18 | 0.14 | 1.65 |
| 6 | 0.94 | 0.03 | 3.39 | 0.36 | 0.18 | 1.61 |
| 7 | 0.98 | 0.03 | 3.26 | 0.33 | 0.12 | 1.69 |
| 8 | 0.95 | 0.03 | 3.64 | 0.38 | 0.17 | 1.97 |
| 9 | 0.97 | 0.04 | 2.06 | 0.21 | 0.12 | 1.20 |
| 10 | 0.98 | 0.03 | 3.43 | 0.35 | 0.14 | 1.56 |
| 11 | 0.98 | 0.04 | 3.00 | 0.31 | 0.18 | 1.77 |
| 12 | 0.95 | 0.04 | 1.73 | 0.18 | 0.13 | 1.22 |
| 13 | 0.94 | 0.06 | 8.68 | 0.92 | 0.90 | 3.26 |
| 14 | 0.80 | 0.17 | 0.99 | 0.12 | 0.82 | 2.77 |
| 15 | 0.96 | 0.04 | 2.03 | 0.21 | 0.11 | 1.74 |
| 16 | 0.90 | 0.10 | 0.92 | 0.10 | 0.22 | 1.27 |

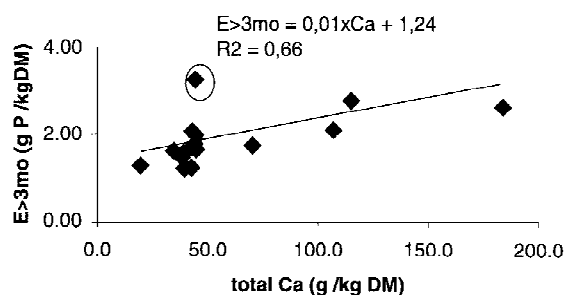


Figure 3. Relation between the total Ca content (total Ca) and the calculated amount of Pi which can not be isotopically exchanged within 3 months ($E_{>3mo}$) in the studied composts. The correlation equation was calculated without the encircled point of compost 13, which was the only compost with a pH lower than 7.

$E_{>3mo}$ and total Al ($r^2=0.42$). These results suggest that in the alkaline composts studied in this work the amount of slowly exchangeable Pi was controlled by the total amount of P and Ca present. Finally, no relationship could be observed between $E_{1min-3mo}$ and any of the compost properties shown in Table 2.

Sequential extraction of inorganic P in 4 composts

Almost all the inorganic P was sequentially extracted from the 4 compost samples 1, 2, 8 and 14 (Table 4).

The amount of water-extractable Pi ranged between 3.2 and 19.6% of the total Pi content. The amount of bicarbonate-extractable Pi varied between 26.1 and 34.5%, NaOH-extractable Pi varied between 7.9 and 24.8% and HCl-extractable Pi varied between 31.3 and 50.5% of the total Pi. The proportion of Pi which could not be extracted by this sequential procedure did not exceed 10%.

These results suggest that about 30 to 50% of the total Pi in these composts is rapidly plant-available (Pi extracted by water and bicarbonate), which confirms the high solubility of compost-Pi in water or saline solutions already observed for different compost types by Inbar et al. (1993), Kuo et al. (1999) and Traore et al. (1999). However, air-drying the compost samples prior to the sequential extraction might have resulted in an overestimation of the proportion of rapidly plant available Pi (Grierson et al., 1998). Furthermore, between 30 and 50% of the total Pi was found in the form of precipitated P-Ca compounds, which parallels the results for alkaline composts of different types obtained by Preston et al. (1986), Alt et al. (1994), and Traore et al. (1999). The highest concentration of HCl-extractable Pi was observed for compost 2, sta-

Table 4. Sequential extraction of inorganic P (g kg⁻¹ DM) in 4 composts

| Compost | 1 | 2 | 8 | 14 |
|--------------------|--------------|-------------|-------------|-------------|
| Extractant | | | | |
| H ₂ O | 0.54 (0.02)* | 0.31 (0.03) | 0.41 (0.01) | 0.12 (0.01) |
| NaHCO ₃ | 0.74 (0.02) | 0.78 (0.01) | 0.87 (0.03) | 0.99 (0.01) |
| NaOH | 0.40 (0.01) | 0.27 (0.03) | 0.20 (0.01) | 0.92 (0.06) |
| HCl | 0.86 (0.06) | 1.51 (0.14) | 0.91 (0.15) | 1.32 (0.15) |
| Residual Pi | 0.21 | 0.12 | 0.13 | 0.36 |

*Each value is the mean of four replicates, standard deviation in brackets.

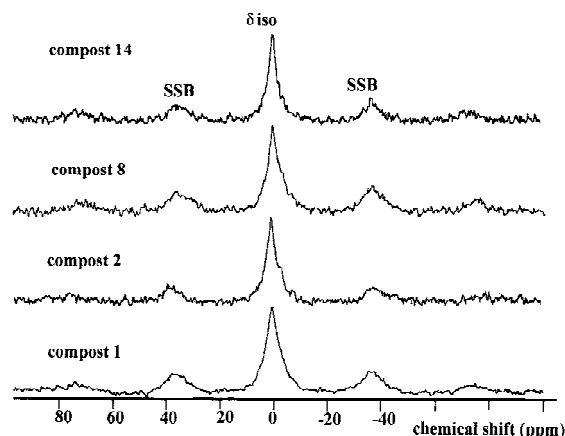


Figure 4. MAS ³¹P NMR spectra of four composts (isotropic chemical shift δ_{iso} ; spinning side bands SSB) obtained with the single pulse (SP) sequence. Chemical shifts are relative to external 85% aqueous H₃PO₄ at 0 ppm.

bilized with lime, which probably led to an increased precipitation of P-Ca compounds.

Solid-State MAS³¹P NMR spectroscopy

The MAS ³¹P NMR spectra of the four unextracted compost samples 1, 2, 8 and 14 obtained with the single pulse sequence (SP) are very similar (Figure 4). Considering that S/N increases with the square root of the number of scans (NS), the much higher number of scans needed to obtain a spectrum for compost 1 with a signal to noise ratio similar to the S/N ratio obtained with the 3 other composts (Tables 5 a & b) confirm qualitatively the lower total P content of compost 1 measured in wet chemistry (Table 2). All spectra exhibit a broad signal with isotropic chemical shifts δ_{iso} between 2.7 and 3.4 ppm. In case of the composts 2, 8 and 14, shoulders located upfield of the main signal are observed between 0 and -5 ppm. The spinning side bands (SSB) indicate that the MAS fre-

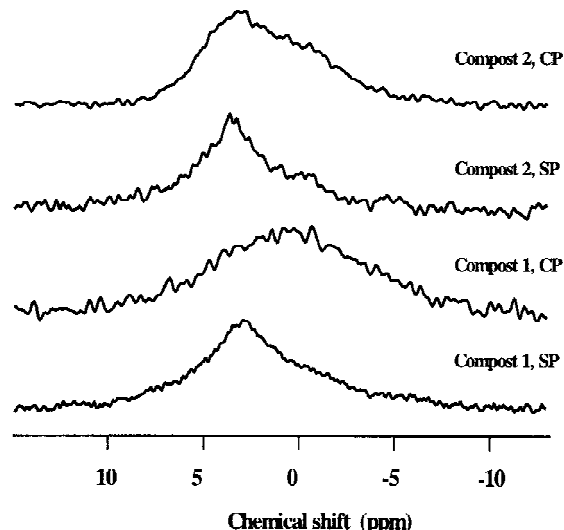


Figure 5. Comparison of the MAS ³¹P NMR spectra of unextracted composts 1 and 2 obtained with the single pulse (SP) and cross polarization (CP) sequences. Chemical shifts are relative to external 85% aqueous H₃PO₄ at 0 ppm.

quency of 8 kHz is small compared to the ³¹P chemical shift anisotropy of the samples (Figure 4). The half-width $\Delta\nu_{1/2}$ of the peaks varies for the four composts between 469 and 849 Hz. In the cross polarization (CP) sequence a symmetric broad resonance ($\Delta\nu_{1/2}$ of 1507 Hz) is observed for compost 1 at δ_{iso} of 0.4 ppm (Figure 5). For compost 2 an asymmetric peak is observed with $\Delta\nu_{1/2}$ of 1128 Hz and δ_{iso} of 2.9 ppm with a shoulder at 0 ppm. Obviously for both samples, the group of P sites at higher field is faster polarized, assuming that the contact time of 2 ms is short with respect to the proton-phosphorus distance of two and more bonds.

The different extractants used in the sequential extraction had little effect on the SP and CP spectra obtained for compost 1 (Table 5a). The only clear trend

Table 5a. MAS ^{31}P NMR results (chemical shift δ_{iso} ; peak width at half height $\Delta\nu_{1/2}$; number of scans NS; signal/noise ratio X: 1) obtained with single pulse (SP) and cross polarization (CP) sequences for compost 1 after various steps of the sequential extraction. Chemical shifts are referenced to aqueous 85% H_3PO_4 at 0 ppm. For noise reduction without window function the first 256 time domain data points (TD_{used}) of the free induction decay (2 k) were Fourier transformed into 16 k data points (8 k real part)

| Compost | Extraction sequence | Sequence | δ_{iso} (ppm) | $\Delta\nu_{1/2}$ (Hz) | NS | Signal/noise ratio (X) | Rotation frequency (kHz) |
|----------------|---|----------|-------------------------|---------------------------|-------|---------------------------|-----------------------------|
| 1 | unextracted | SP | 2.7 | 849 | 2621 | 27 | 6 |
| 1 | unextracted | CP | 0.4 | 1507 | 12587 | 15 | 8 |
| 1 | H ₂ O | SP | 2.7 | 692 | 2615 | 55 | 6 |
| 1 | H ₂ O | CP | 0.4 | 1359 | 16384 | 23 | 8 |
| shoulder at -5 | | | | | | | |
| 1 | H ₂ O and NaHCO ₃ | SP | 2.1 | 898 | 713 | 12 | 6 |
| 1 | H ₂ O, NaHCO ₃ | CP | 2.9 | 1640 | 16384 | 13 | 8 |
| 1 | H ₂ O, NaHCO ₃ and NaOH | SP | 2.6 | 758 | 3072 | 23 | 6 |
| 1 | H ₂ O, NaHCO ₃ and NaOH | CP | 0 | 1535 | 16384 | 7 | 8 |

Table 5b. MAS ^{31}P NMR results (chemical shift δ_{iso} ; peak width at half height $\Delta\nu_{1/2}$; number of scans NS; signal/noise ratio X: 1) obtained with single pulse (SP) and cross polarization (CP) sequences for compost 2 after various steps of the sequential extraction and for composts 8 and 14. Chemical shifts are referenced to aqueous 85% H_3PO_4 at 0 ppm. For noise reduction without window function the first 256 time domain data points (TD_{used}) of the free induction decay (2 k) were Fourier transformed into 16 k data points (8 k real part)

| Compost | Extraction sequence | Sequence | δ_{iso} (ppm) | $\Delta\nu_{1/2}$ (Hz) | NS | Signal/noise ratio (X) | Rotation frequency (kHz) |
|---------|---|----------|--|---------------------------|-------|---------------------------|-----------------------------|
| 2 | unextracted | SP | 3.4 shoulder between 0 and -4 | 594 | 368 | 18 | 6 |
| 2 | unextracted | CP | 2.9 shoulder at -0.2 | 1128 | 16384 | 33 | 8 |
| 2 | H ₂ O | SP | 3.0 shoulder between -1 and -7 | 441 | 2048 | 85 | 7 |
| 2 | H ₂ O | CP | 3.5 shoulder at 0.2 | 929 | 2048 | 16 | 7 |
| 2 | H ₂ O and NaHCO ₃ | SP | 2.7 shoulder at -1.3 | 677 | 618 | 32 | 6 |
| 2 | H ₂ O and NaHCO ₃ | CP | 1.2 shoulder at -2.8 | 1229 | 16348 | 23 | 8 |
| 2 | H ₂ O, NaHCO ₃ and NaOH | SP | 2.7 | 716 | 2836 | 33 | 6 |
| 2 | H ₂ O, NaHCO ₃ and NaOH | CP | 0 | 1494 | 16384 | 9 | 8 |
| 8 | unextracted | SP | 2.9 shoulder between 0 and -5 | 714 | 368 | 18 | 6 |
| 14 | unextracted | SP | 3.2 shoulder between 1 and -5 | 469 | 368 | 23 | 6 |

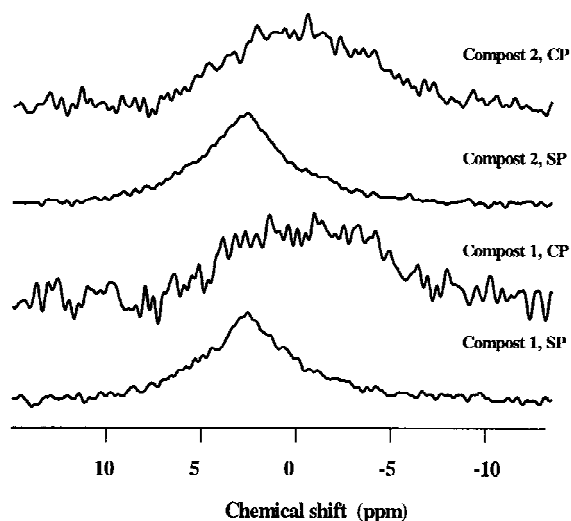


Figure 6. Comparison of the MAS ^{31}P NMR spectra of composts 1 and 2 extracted successively with H_2O , NaHCO_3 and NaOH obtained with the single pulse (SP) and cross polarization (CP) sequences. Chemical shifts are relative to external 85% aqueous H_3PO_4 at 0 ppm.

is a decrease of the S/N ratio for the same number of scans in the CP sequence between the sample extracted with H_2O and the sample extracted with H_2O , NaHCO_3 and NaOH whereas in the SP sequence the S/N ratio of the unextracted sample was not different from that of the sample extracted with H_2O , NaHCO_3 and NaOH . This result suggests that the sequential extraction caused a larger extraction of rapidly polarizable ^{31}P nuclei from the solid than of slowly polarizable P.

For the extracted samples of compost 2 the δ_{iso} value has a trend to higher field, indicating that a low field component of P has been extracted (Table 5b). Finally, both the SP and CP sequences show that the shoulder located in the unextracted sample of compost 2 upfield of the main signal between 0 and -4 ppm disappears after the NaOH extraction (Figures 5 and 6).

According to the higher S/N observed for compost 2 with comparable scan numbers the amount of unextracted P remains higher in this compost after each step of the extraction than in compost 1. Obviously compost 1 contains more P which is extractable with H_2O , NaHCO_3 as well as with NaOH than compost 2 confirming the results obtained with wet chemistry (Table 4).

The natural hydroxyapatite and the fluoroapatites studied as reference compounds have δ_{iso} values

Table 6. MAS ^{31}P NMR results (chemical shift δ_{iso} ; peak width at half height $\Delta\nu_{1/2}$) obtained for the reference compounds (CP sequence: contact time 1 ms, relaxation delay 5 s; rotation frequency 8 kHz, except for DNA (7 kHz)). Chemical shifts are referenced to aqueous 85% H_3PO_4 at 0 ppm. The free induction decays (4 k time domain data points, TD) were Fourier transformed into 16 k data points (8 k real part)

| Compound | δ_{iso} (ppm) | $\Delta\nu_{1/2}$ (Hz) |
|---|-------------------------|---------------------------|
| $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ (DCDP) | 1.1 | 93 |
| | -1.8 ^{a)} | |
| | -7.7 | 77 |
| $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ (MCP) | -0.3 | 185 |
| | -4.7 | 170 |
| Hydroxyapatite (OHA) | 2.2 | 249 |
| Fluoroapatite 1 (FA1) | 2.7 | 316 |
| Fluoroapatite 2 (FA2) | 2.5 | 125 |
| Fluoroapatite 3 (FA3) | 2.0 | 342 |
| | -10.9 | 286 |
| Myoinositol Hexaphosphate (I6P) | -2.1 | 1130 |
| Deoxyribonucleic acid (DNA) | -1.0 | 566 |

a) Partly resolved.

between 2.0 and 2.7 ppm (Table 6) which are in the range of the δ_{iso} values observed for natural and synthetic condensed calcium phosphates such as octacalciumphosphate, hydroxy-, fluoro- and carbonatoapatites (Rothwell et al., 1980; Aue et al., 1984; Belton et al., 1988; Wu et al., 1994; Vogel et al., 1996). These results suggest that a large fraction of compost-Pi is present in the form of condensed calcium phosphates such as apatites or octacalcium phosphates. The sequential extraction gives results consistent with this assignment since δ_{iso} of the solid residues with the SP sequence remains between 2.1 and 3.0 after NaOH -extraction (Tables 5a & b; Figure 6). These condensed calcium phosphates are neither soluble in water nor in bicarbonate and NaOH . The extraction of ^{31}P nuclei with δ_{iso} ranging from 2.7 and 3.4 ppm from compost 2 during the sequential extraction (Table 5b) suggests that P-Ca rich colloidal materials were also removed during the extraction. The reference compounds for organic P species (DNA and I6P) studied exhibit chemical shifts δ_{iso} of -1.0 and -2.1 ppm (Table 6). These are in the range of chemical shifts of various organic P compounds measured in the liquid state (Pant et al., 1999). Therefore, the shoulder located upfield from the main peak of the composts could be assigned to the presence of organic P species.

This assignment is consistent with the disappearance of this shoulder after the NaOH extraction since organic P compounds are soluble in NaOH. Finally, the presence of soluble orthophosphates such as monocalcium phosphate is also probable since its δ_{iso} is around 0 ppm (Table 6). The broad signals observed with the CP sequence show that a large proportion of the ^{31}P nuclei is located in the close vicinity of ^1H nuclei, in agreement with the presence of protons in all of the P species assigned above.

The half-width $\Delta\nu_{1/2}$ of the peaks gives also relevant information. The $\Delta\nu_{1/2}$ observed for the compost samples before and after extraction is much larger than that of natural apatites (Table 6), which itself is much larger than $\Delta\nu_{1/2}$ reported for synthetic crystallized calcium phosphates (Belton et al., 1988). This could be related (i) to the structural inhomogeneity of the ^{31}P nuclei present in the compost samples (i.e. to the presence of a mixture of P species each with a large number of different magnetic sites), (ii) to the presence of poorly ordered minerals and (iii) to the presence of paramagnetic impurities (e.g. Fe, Table 2) or most probably to a combination of these three origins. This reasoning suggests then that the P-Ca species present in composts are not well crystallized as observed by Frossard et al. (1994) on sludge-P, and is coherent with the known ability of organic substances to inhibit the crystallization of apatites or octacalcium phosphates (Inskeep and Silvertooth, 1988).

Conclusions

The different approaches used in this investigation (isotopic exchange, sequential extraction and solid-state ^{31}P NMR) demonstrate the presence of a complex mixture of inorganic P species Pi in the studied composts.

Solid-state MAS ^{31}P NMR results strongly suggest in alkaline composts the presence of a range of scarcely soluble and ill-crystallized Ca-P compounds such as apatites or octacalcium phosphates. This evidence, together with the correlation observed between total Ca in the 15 alkaline composts (all except compost 13) and the amount of Pi which can not be isotopically exchanged within 3 months, suggests that the slowly or non-exchangeable Pi in these composts is bound to Ca in the form of apatites or octacalcium phosphates. From an agronomic point of view this fraction of compost-P will probably have a low availability to plants in neutral and alkaline soils (Fardeau

et al., 1988). Isotopic exchange experiments and sequential extraction show that the composts contain relatively large concentrations of rapidly available Pi confirming results obtained in previous studies (Inbar et al., 1993; Kuo et al., 1999; Traore et al., 1999). The amount of water-soluble Pi, and the amount of P isotopically exchangeable in 1 min are correlated with the total N, C and P content. These relations could be due to: (i) the composition of the organic wastes themselves since these are the original sources of N and P of the composts, (ii) the presence of organic substances which can inhibit the precipitation of Pi in insoluble forms such as apatite or octacalcium P (Inskeep and Silvertooth, 1988), and/or (iii) to mineralisation of organic and microbial P caused by air-drying the composts before analysis (Grierson et al., 1998). The strong correlation between total N and Cp allows the use of total N to predict for this type of compost the amount of rapidly plant-available Pi. However, since during their preparation composts can be subjected to drying and rewetting cycles, their effect on organic and microbial P mineralisation, and more generally on orthophosphate release should be further studied.

Acknowledgements

The authors thank J. Fuchs (Frick, Switzerland) and K. Schleiss (Baar, Switzerland) for their help in selecting the compost samples, C. Faisse (ENSAIA, Nancy, France) for assistance, Dr. P. Brack (Department of Earth Sciences, ETH Zurich, Switzerland) for lending the apatites used as references, and the Research Commission of the ETH Zurich for financial support.

References

- Alt D, Peters I & Fokken H (1994) Estimation of phosphorus availability from composts and compost/peat mixtures by different extraction methods. *Comm Soil Sci Plant Anal* 25: 2063–2080
- Aue WP, Roufosse AH, Glimcher MJ & Griffin RG (1984) Solid state phosphorus 31 nuclear magnetic resonance studies of synthetic solid phases of calcium phosphate: Potential models of bone minerals. *Biochem J* 23: 6110–6114
- Belton PS, Harris RK & Wilkes PJ (1988) Solid state phosphorus 31 NMR studies of synthetic inorganic calcium phosphates. *J Chem Solids* 49: 21–27
- Bezzola LC, Lopez SC & Barbaro NO (1994) Effectiveness of different phosphatic fertilizers measured using labelled superphosphate and phosphorus taken up by plants. *Fert Res* 39: 31–37
- Candinas T, Golder E, Kupper T & Besson JM (1999) Nähr- und Schadstoffe im Kompost. *Agrarforschung* 6: 421–424

- Fardeau JC (1996) Dynamics of phosphate in soils. An isotopic outlook. *Fert Res* 45: 91–100
- Fardeau JC, Morel C & Jahiel M (1988) Does long contact with the soil improve the efficiency of rock phosphate? Results of isotopic studies. *Fert Res* 17: 3–19
- Frossard E, Tekely P & Grimal JY (1994) Characterization of phosphate species in urban sewage sludges by high resolution solid state ^{31}P NMR. *Eur J Soil Sci* 45: 403–408
- Frossard E, Sinaj S & Dufour P (1996) Phosphorus in sewage sludges as assessed by isotopic exchange. *Soil Sci Soc Am J* 60: 179–182
- Gigliotti G, Businelli D & Giusquiani PL (1999) Composition changes of soil humus after massive application of urban waste compost: a comparison between FT-IR spectroscopy and humification parameters *Nutr Cycl Agroecosyst* 55: 23–28
- Grierson PF, Comerford NB & Jokela EJ (1998) Phosphorus mineralization kinetics and response of microbial phosphorus to drying and rewetting in a Florida Spodosol. *Soil Biol Biochem* 30: 1323–1331
- Hadas A, Krautsky L & Portnoy R (1996) Mineralization of composted manure and microbial dynamics in soil as affected by long-term nitrogen management. *Soil Biol Biochem* 28: 733–738
- Inbar Y, Hadar Y & Chen Y (1993) Recycling of cattle manure: the composting process and characterization of maturity. *J Environ Qual* 22: 857–863
- Inskeep WP & Silvertooth JC (1988) Inhibition of hydroxyapatite precipitation in the presence of fulvic, humic and tannic acids. *Soil Sci Soc Am J* 52: 941–946
- John MK (1970) Colorimetric determination of phosphorus in soil and plant materials with ascorbic acid. *Soil Sci* 109: 214–220
- Kuhn E, Eugster A & Arnet R (1996) Nährstoffgehalte von Komposten aus aargauischen Anlagen. *Agrarforschung* 2: 81–84
- Kuo S, Hummel RL, Jellum EJ & Winters D (1999) Solubility and leachability of fishwaste compost phosphorus in soilless growing media. *J Environ Qual* 28: 164–169
- Pant HK, PR Warman & Nowak J (1999) Identification of soil organic phosphorus by ^{31}P nuclear magnetic resonance spectroscopy. *Commun Soil Sci Plant Anal* 30: 757–772
- Pommel B (1982) Aptitude de plusieurs déchets urbains à fournir du phosphore aux cultures. *Agronomie* 2: 851–857
- Preston CM, Ripmeester JA, Mathur SP & Levesque M (1986) Application of solution and solid state multinuclear NMR to a peat based composting system for fish and crab scrap. *Can J Spectrosc* 31: 63–69
- Rothwell WP, Waugh JS & Yesinowski JP (1980) High resolution variable temperature ^{31}P NMR of solid calcium phosphates. *J Am Chem Soc* 102: 2637–2643
- Saunders WMH & Williams EG (1955) Observations on the determination of total organic phosphorus in soils. *J Soil Sci* 6: 254–267
- Sikora LJ & Yakovchenko V (1996) Soil organic matter mineralization after compost amendment. *Soil Sci Soc Am J* 60: 1401–1404
- Sikora LJ, Tester CF, Taylor JM & Parr JF (1982) Phosphorus uptake by fescue from soils amended with sewage sludge compost. *Agron J* 74: 27–32
- Sinaj S, Traore O & Frossard E (2001) Effect of compost and soil properties on the availability of compost phosphate for white clover (*Trifolium repens* L.). *Nutr. Cycl. Agroecosyst.* 62: 89–102
- SYSTAT for windows (1996) Statistics version 6.0. SPSS Inc, USA
- Traore O, Sinaj S, Frossard E & Van de Kerkhove JM (1999) Effect of composting time on phosphate availability. *Nutr Cycl Agroecosyst* 55: 123–131
- Vogel J, Rüssel C, Günther G, Hartmann P, Vizethum F & Bergner N (1996) Characterization of plasma-sprayed hydroxyapatite by ^{31}P -MAS-NMR and the effect of subsequent annealing. *J Mater Sci Mater Med* 7: 495–499
- Warman PR, Muizelaar T & Termeer WC (1995) Bioavailability of As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Se, and Zn, from biosolids amended compost. *Compost Sci Util* 3: 40–50
- Wen G, Bates TE, Voroney RP, Winter JP & Schellenbert MP (1997) Comparison of phosphorus availability with application of sewage sludge, sludge compost and manure compost. *Comm Soil Sci Plant Anal* 28: 1481–1497
- Wen G, Bates TE, Voroney RP, Winter JP & Schellenberg MP (1999) Influence of application of sewage sludges, and sludge and manure composts on plant Ca and Mg concentration and soil extractability in field experiments. *Nutr Cycl Agroecosyst* 55: 51–61
- Wu Y, Glimcher MJ, Rey C & Ackerman JL (1994) A unique protonated phosphate group in bone mineral not present in synthetic calcium phosphates. Identification by phosphorus-31 solid state NMR spectroscopy. *J Mol Biol* 244: 423–435